Fuel 220 (2018) 446–452

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Semi-clathrate hydrate process of methane in porous media-mesoporous materials of SBA-15

Jianzhong Zhao[a,b,*], Yangsheng Zhao[a,b,*], Weiguo Liang[b,c], Su Song[d], Qiang Gao[a]

[a] *Mining Technology Institute, Taiyuan University of Technology, Taiyuan 030024, PR China*
[b] *Key Laboratory of In-situ Property Improving Mining of Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, PR China*
[c] *College of Mining Engineering, Taiyuan University of Technology, Taiyuan 030024, PR China*
[d] *Department of Mechanical Engineering, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan*

ARTICLE INFO

Keywords:
SBA-15
Semi-clathrate hydrate
Tetrahydrofuran(THF)
Tetra-n-butyl ammonium bromide (TBAB)
Formation

ABSTRACT

The hydrate based technology process in porous media is an effective method for gas storage and separation. The formation of methane hydrate in SBA-15, an ordered mesoporous silicon material, was measured with tetrahydrofuran (THF) and tetra-n-butyl ammonium bromide (TBAB) aqueous solution at different pressure and temperature·THF and TBAB were selected to lower the equilibrium pressure at which the gas hydrates can efficiently formed. At the experimental condition of 1.8 MPa–2.0 MPa, SBA-15 was proved to be effective to methane uptake in the hydrates. The results showed that mesoporous silica can help to get the fast-kinetic formation of methane hydrates. The temperature was almost steady and only had two slight increase no more than 0.5 K. The pressure dropped rapidly and then became gentle, which translated into an increase in gas uptake rapidly in the beginning of 100 min and then maintained stable till the end. The reaction rate quickly reached the peak then rapidly dropped and slowly decayed. The desirable kinetics parameters of final gas uptake capacity, average of reaction rate and conversion of gas to hydrate (%) were obtained at higher pressure and lower temperature while THF was better than TBAB. A gas uptake capacity of 91.13 mmol methane gas per mole water was achieved when the hydrates were formed in the presence of THF with SBA-15.

1. Introduction

Gas hydrates (or clathrate hydrates) are non-stoichiometric ice-like solid compounds consisting of gas molecules and water molecules [1,2]. Generally, gas hydrates have three basic crystal structures (structure I, structure II, and structure H) where gas molecules (guest molecules) are enclathrated in cavity structures that are formed by hydrogen-bonded water molecules (host molecules) [3,4]. Methane hydrates are formed at high pressure and low temperature with solid crystalline structure that is made of hydrogen bonded water cages in which a methane molecule is encaged [5,6]. Upon dissociation, one volume of solid methane hydrates can release 150–180 volumes methane gases at a standard temperature and pressure (STP) [7]. Gas hydrates have very unique properties of heat-mass transfer and are being applied in many areas such as the gas storage, separation [8] and capturing medium [9–11].

However, the large-scale application of methane hydrates has been hindered by a few practical problems, including the slow formation kinetics of gas hydrates and low gas uptake capacity [12]. Increasing hydrates formation rate might compromise the gas capacity, therefore reducing its effectiveness [13]. The un-reacted interstitial water trapped between solid hydrates particles is also another problem, which occupies a large percentage of the total volume, therefore not only increases the maintenance cost but also decreases the gas uptake capacity [14]. There are two approaches to overcome the slow kinetics of hydrate formation: the first approach is innovative reactor designs including the use of different porous media and the second approach is the use of kinetic promoters (predominantly surfactants) in order to enhance the rate of hydrate formation [15]. Many studies have been carried out to improve the kinetics of hydrate formation by enhancing the mass and heat transfer during the hydrate formation process in different materials [16,17]. Some researchers have used porous media to make water molecules scatter on the pore surfaces of the materials [18,19], which increases the contact area of the gas and water, thereby accelerating gas hydrate formation [20–22]. Zhou et al. have reported that using water-wetted activated carbon can promote the rate of natural gas hydrate formation, reduce the equilibrium pressure, and save costs [23,24]. Especially, over the last 10 years, there has been growing interest in new materials engineering methods for enhancing the rate of gas hydrate formation, which involved in sand packs [25–27], hollow

---

[*] Corresponding authors at: Mining Technology Institute, Taiyuan University of Technology, Taiyuan 030024, PR China.
E-mail addresses: zhaojianzhong@tyut.edu.cn (J. Zhao), y-s-zhao@263.net (Y. Zhao).

https://doi.org/10.1016/j.fuel.2018.01.010
Received 30 September 2017; Received in revised form 20 November 2017; Accepted 3 January 2018

silica [28], and hydrogels [29]. A common observation in all of these studies was that the rate of gas hydrate formation increased as the water saturation was decreased [30,31]. Though the kinetics of hydrate formation is improved by a choice of suitable reactor design or kinetic promoter, there is no reduction of the high energy requirement due to low temperature and high-pressure conditions of hydrate formation. However, some problems still need to be studied. For example, how to choose appropriate promoters to further reduce the hydrate formation pressure, and what changes will happen to the structure of hydrates after adding the promoter [32–34]. The most important is what size of pore structure is the most suitable for hydrate formation and application.

Apart from different materials, different thermodynamic and kinetic promoters are being evaluated for improving the hydrate formation conditions and the kinetics respectively [35]. The presence of THF or TBAB can significantly shift the hydrate phase equilibrium to lower pressure for flue gas mixtures ($CH_4/CO_2/N_2$). Especially, some major advances have been achieved on mixed hydrate formation in the presence of additive likes THF whereby there is no need for even the addition of any materials as THF can do both the job of providing thermodynamic and kinetic promotion [36]. THF can form structure II (S-II) hydrates with water and small molecules such as CH_4, CO_2 or N_2 while TBAB forms the title semi-clathrate hydrate crystal, $C_{16}H_{36}N^+ \cdot Br^- \cdot 38H_2O$ [37]. There has been a series of works on the use of bio-friendly amino acids to promote the methane hydrate formation got better enhancement of methane hydrate formation [38,39]. But the thermodynamic promoter can enter the clathrate cage, resulting in a penalty on the storage capacity of methane is inevitable. Thus, a hybrid combination approach is required to address all the major challenges of the hydrate technology process chain wherein the improvement in kinetics of hydrate formation along with milder hydrate storage conditions is necessary.

Ordered mesoporous silica (pores diameters between 2 and 50 nm) has been brought to academic attention due to its unique properties compared to dense materials [40,41], for example, SBA-15 with a 2-D hexagonal structure have high surface-area-to-volume ratios, which may make them more reactive due to their mesoporous structures. Such mesoporous silica powders have been used for catalysis in chemical engineering [42]. Hydrate formation in the mesoporous space is a new attempt which can reduce gas hydrate formation pressure by adding promoter. Theoretically, the mesoporous silica not only can accommodate adsorption sites for molecule of methane and water on its surface, but also helps the fast-kinetic formation of methane gas hydrates. Hence, the formation of methane hydrates was examined in ordered mesoporous silicon SBA-15 at the different promoters and pressure-temperature condition. Kinetics of methane hydrate formation for TBAB and THF aqueous systems had been investigated at an initial pressure conditions of 2.0 and 1.8 MPa and at 279.15 K and 282.15 K with SBA-15.

2. Experiment

2.1. Experimental apparatus

Experiments were carried out on a setup schematically shown in Fig. 1. Water saturated mesoporous silicon SBA-15 was packed into a tube reactor of length 1000 mm and inner diameter 11.0 mm. The pressure transducer was bought from Micro Sensor Co., Ltd., the type is MPM480 and the precision is 0.01 MPa. The thermocouples were supplied by Beijing Kunlun Ocean Instrument Company Ltd., the type is KYW-T1 and the precision is ± 0.01 K. The zero point of transducers was adjusted automatically to compensate for the fluctuation of room temperature. There were eight thermocouples set along the tube reactor to record the distribution of temperature. All parts were connected by stainless steel capillary tubes of inner diameter 2.0 mm and wall thickness is 0.5 mm. The computer recorded the variation of signals with time and issued commands of experiments according to a prescribed program.

2.2. Materials

Mesoporous silicon is porous media and also as promoting media for methane hydrate formation. SBA-15 was supplied by Jiaxing Tanli new materials R&D Co., Ltd. Table 1 listed the detailed related properties of SBA-15 which were provided by the manufacturer and several important pore properties have been characterized in Section 3.1.

In the present analysis, deionized water and 99.9% methane gas (Beijing AP BAIF Gases Industry Co., LTD, Beijing, China) were used.

THF was purchased from Tianjing Beicheng Chemical Co., Ltd., with a certified mass purity higher than 99%. THF was dissolved in deionized water to form THF solutions with concentrations of 5.56 mol %. (The theoretical proportion of the semi-clathrate hydrates, THF: $H_2O = 1:17$)

Analytical-grade TBAB with the purity of 99.0 mol% was from Tianjing Fucheng Chemicals Ltd. TBAB was dissolved in deionized water to form TBAB solutions with concentrations of 2.56 mol %. (The best proportion of the semi-clathrate hydrates theory, $C_{16}H_{36}N^+ \cdot Br^- \cdot 38H_2O$)

THF or TBAB solution with desired concentration was then slowly added to the SBA-15 by mechanical mixing to prepare the wet sample.

2.3. Experimental procedure

Firstly, after the reactor was cleaned and dried, the mesoporous silicon SBA-15 presaturated with aqueous solution of THF or TBAB were introduced into the tube reactor. After that, the reactor was connected with the gas pipeline and put into the water bath.

Subsequently, the reactor was purged with methane gas to a pressure of 0.5 MPa three times to remove residual air in the porous. Following that, the reactor compartment was pressurized to experimental pressure with CH_4 gas and allowed to stabilize at 290 K under conditions outside the hydrate equilibrium region.

After the stabilization of pressure and temperature, the reactor was cooled to predetermined temperature of water bath. Exothermic methane hydrate formation is distinguished by an increase in temperature accompanied with drastic pressure drop. Once the pressure and temperature within the reactor stabilized around the set point, the desired hydrate was attained, and hydrate formation stage was considered complete. In this case, the volume and the bath temperature are constant while the pressure decreased during the experiment. As the cell temperature is lowered the pressure decreases, principally due to gas contraction as well as increased gas solubility upon cooling at constant volume. Neither gas nor water were added to the system during the experiment. During the whole hydrate formation process, the temperature and pressure were recorded by the data collection system.

2.4. Calculation of kinetics and gas uptake capacity

In the beginning, the pressure of the reactor dropped continuously due to the enclathration of methane into the hydrate cages. Hydrate formation is considered complete when the pressure of the reactor system stabilized with no further drop [43]. At the beginning, amount of methane gas was introduced into the reactor $n_{g,0}$ is calculated from Eq. (1):

$$n_{g,0} = \frac{P_0 V_g}{z_0 R T_{0,avg}} \tag{1}$$

where P_0 is the pressure in the reactor, V_g is the volume of reactor by which methane gas occupies, z_0 is the compressibility factor at P_0 and $T_{0,avg}$ computed using Pitzer correlations, R is the universal gas constant and $T_{0,avg}$ is the average temperature over all measured points within